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<b>(21) International Application Number:</b> PCT/BE98/00099 <b>(22) International Filing Date:</b> 26 June 1998 (26.06.98) <b>(30) Priority Data:</b> 97870107.6 15 July 1997 (15.07.97) EP <i>(34) Countries for which the regional or international application was filed:</i> BE et al. <b>(71) Applicant (for all designated States except US):</b> METALS & CHEMICALS [BE/BE]; 94, rue Tenbosch, B-1050 Brussels (BE). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> HAJI, Anas [BE/BE]; Avenue P. VanderBiest 37, Boîte 168, B-1150 Brussels (BE). <b>(74) Agents:</b> VAN MALDEREN, Joëlle et al.; Office Van Malderen, Place Reine Fabiola 6/1, B-1083 Brussels (BE).		<b>(81) Designated States:</b> AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, DE, DE (Utility model), EE, GE, GW, HU, ID, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> CEMENTITIOUS POLYMERIC MATRIX COMPRISING SILICA ALUMINOUS MATERIALS		
<b>(57) Abstract</b> <p>The present invention is related to a cementitious matrix consisting essentially of aluminosilicate polymer comprising: a liquid component form of alkali metal silicate aqueous solution of formula <math>M_2O.RSiO_2.XH_2O</math>, in which: M is an alkali metal monovalent cation such as <math>K^+</math> or <math>Na^+</math>; R is designated to be the molar ratio of <math>SiO_2/M_2O</math> range comprised between 0.5/1 and 9/1; and X is the amount of water comprised between 30 and 70 wt.%; a powder component form which comprises at least: silico-aluminous reactive raw materials composed of <math>Al_6Si_2O_{13}</math> and <math>Al_2O_3.4 SiO_2</math>, with a relative proportion ranging from 40 to 60 wt.%, the particle size of both components ranging from 50 to 70 microns; zirconium silicate flour having a particle size ranging from 50 to 70 microns.</p>		

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CEMENTITIOUS POLYMERIC MATRIX COMPRISING SILICA ALUMINOUS  
MATERIALS

10

Field of the invention

The present invention is related to a cementitious polymeric matrix comprising silica aluminous materials having high mechanical properties and high  
15 temperature resistance properties.

The present invention is also related to a method of realisation of such a cementitious polymeric matrix comprising silica aluminous materials.

20 Background of the invention

Heat and fire resistance silica products traditionally have been prepared by energy-intensive methods that require costly high consumption of energy and carefully regulated chemical formulation, pre-heating,  
25 firing and cooling cycles to achieve reproducible quality products. Various calcium aluminate and calcined aluminous cement and refractory moulding products have been produced, but none of these has achieved the combined of fast curing, high adhesive bonding qualities, low material  
30 accessibility, together with good mechanical, thermal and chemical properties.

Aims of the present invention

Thus, a need exists for a product that combines the above qualities with simplicity of use so as to preclude any special skill or training to accommodate the product to various uses.

A first aim of the present invention is to suggest a new product which combines properties of high mechanical resistance with high temperature resistance on the same product.

A further aim of the present invention is to suggest a product having low material cost.

A further aim of the present invention is to suggest a realisation method of such a product which has a simplicity of use so as to preclude any special skill or training to accommodate the product to various uses.

Other advantages and properties of the invention related to the product or to the method of realisation will be described hereunder in the description.

20 Main characteristics of the present invention

The present invention relates to an alumino silicate polymer (ASP) matrix which could meet all the above-mentioned requirements.

The product of the present invention comprises two major components, which are :

- a liquid component form of alkali metal silicate aqueous solution of formula  $M_2O.RSiO_2.XH_2O$ , in which :

M is an alkali metal monovalent cation such as  $K^+$  or  $Na^+$ ;

R is designated to be the molar ratio of  $SiO_2/M_2O$  range comprised between 0.5/1 and 9/1; and

X is the amount of water comprised between 30 and 70 wt%;

- a powder component form which comprises at least :
  - silico-aluminous reactive raw materials composed of  $\text{Al}_6\text{Si}_2\text{O}_{13}$  and  $\text{Al}_2\text{O}_3 \cdot 4 \text{SiO}_2$  with a relative proportion ranging from 40 to 60 wt%, the particle size of both components ranging from 50 to 70 microns.

According to a first preferred embodiment, the preferred powder component further comprises:

- zirconium silicate flour having a particle size ranging from 50 to 70 microns, the ratio of the zirconium silicate flour being comprised between 1 and 25 wt% of the powder component.

According to another preferred embodiment, the powder component further comprises:

- pulverised raw materials being a combination of two major components which are:
  - beauxite component having 80 wt%  $\text{Al}_2\text{O}_3$  alumino content and having maximum grain size of 500 microns,
  - chamosite component having 40 wt%  $\text{Al}_2\text{O}_3$  alumino content and having an average grain size comprised between 60 and 100 microns and being of the formula such as  $((\text{Fe}, \text{Al}, \text{Mg})_6(\text{SiAl})_4\text{O}_{10}(\text{OH})_8)$ , the combination of beauxite chamosite components wave ratio ranging from 1/1 to 1/2 and being preferably around 1/2.

Preferably, the ratio of the raw material being comprised between 1 and 25 wt% of the powder component. Alkali metal silicate solution used in the present invention is prepared by direct reaction of alkali metal hydroxide, water ( $\text{H}_2\text{O}$ ) and precipitated silica ( $\text{SiO}_2$ )

through exothermic reactions. This solution can also be prepared in situ.

The required amount of the components which are mixed and the rheology of the (ASP) matrix can be adapted to various processing techniques by the eventual addition of some other filler materials.

Thus the ASP matrix can be :

- a semi-dry friable material, which can be compacted statically or dynamically into its final shape. The shape can be handled without mould prior to hardening ;
- a plastic paste showing cohesion which can be calendered and compacted by rolling or which can be extruded through a die, similar to classical brick making;
- a liquid suspension of particles, which can be casted or injected in a moule.

After shaping, an increase in temperature (below 100 °C) as initial curing is required to accelerate the initial setting, and then stored for another several days as post curing, so finishing the hardening reaction within a few days leading to following advantageous properties :

- the environmental aspects are very positive such as low temperature processing, low cost raw materials, availability of raw materials together with the recycling of waste products;
- high mechanical strength, for instance, compressive strength between 40 MPA to 100 MPA (depending on formulation), and hardness above 8 Mohs;
- the most important properties of alumino-silicate polymer (ASP) materials are surely the absolute fire resistance, thermal and chemical resistance, as well as durability against weathering. It can be worked on by

means of nailing, screwing, sawing and drilling, non conductivity together with the other two main properties.

The use of widely available raw materials and  
5 simple implementation techniques for the obtention of cheap and durable building materials.

The origin of the raw materials is mineral, more precisely silicate materials which are dominantly present in the earth's crust under the shape, for instance  
10 of clays or weathered materials rocks. Several types of pozzolanic materials are very suited, but also industrial waste products such as by-product pozzolans can be used.

Alumino-silicate (ASP) binding composition is always in a two components system having a powder component  
15 form from mineral origin, and a liquid component form which consisting of inorganic catalysts in solution (usually in water). When the components are mixed together, the catalysts break down the structure of the powder component, and subsequently build up an excellent cementitious  
20 polymeric structure through polymerisation or polycondensation or poly aggregation reactions. The structure of (ASP) materials is however totally inorganic polymers. The emphasis of the present invention has been placed on the development of material systems which do  
25 react at low temperatures and at atmospheric pressure, and which do lead to solid ceramic like end-products.

The cementitious property of ASP materials is attributed to the formation of :

- Alkali metal tri aluminate ( $M_6Al_6O_{12}$ )
- 30 - Alkali metal tri silicate ( $M_6Si_8O_{19}$ )
- Alkali metal di silicate ( $M_2Si_2O_5$ )

In this way, the additives are used to obtain materials with typical ceramic properties, in contrast with the traditional high temperature thermal processing route.

This permits saving in energy and processing cost and offers technological advantages and open new horizon towards excellent building materials. Many traditional building materials (i.e. some organic polymer materials and other mineral base fibres), are moving from restriction towards ban, because they are recognised as extremely toxic materials or to be source of cancer. Thus, a need exists to find a replacement for those traditional banded building materials with emphasis on health and economic grounds.

The superior properties of the products of the present invention can be described as the combination of the following requirements :

1. High mechanical strength both in wet and dry conditions
2. High heat and fire resistance
3. Incombustibility
4. Extremely non-conductivity
5. High chemical resistance
6. Excellent water resistance
7. Low coefficient of thermal expansion
8. Low level of firing contraction
9. Low material cost together with simplicity of use

The present invention of alumino-silicate polymer (ASP) matrix seems to meet all these requirements.

Although the specific properties of the alumino-silicate polymer (ASP) depend on the type of raw materials and additives, there are common features : hardness, stiffness, stability against weathering, chemical, heat and fire.

These properties are the required properties for an excellent construction material. The utilisation field of (ASP) materials is quite wide. It can be used as :

- roofing sheets;
- 5 - low cost insulation panels;
- low density sandwich elements;
- coating surface;
- wear resistant tiles;
- high strength building elements;
- 10 - laminates;
- flexible laminates.

The setting process of ASP binding composition involves a considerable redistribution of the constituents of the solid component form into the  
15 interstitial space occupied by inorganic solution. Thus, the polyaggregation of ASP is essentially a two-stage process in which a gelatinous layer is initially formed on the surface of the alkali metal silicate particles. After the initial setting time, this gel layer begins to spread  
20 fibrillar outgrowths which may actually be tubes, and can radiate from each grain into the interstitial space. This can be compared to the growth of silicate tress that are formed when a piece of metal or a crystal of a metal salt is placed in a solution of sodium silicate. The fibrils  
25 rapidly increase in length and number, and gradually become closely enmeshed.

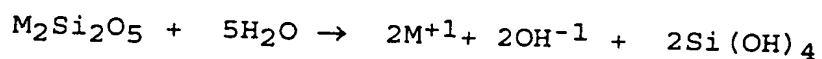
Possibly, the lengthways growth ceases and the fibrils begin to join up sideways so that finally striated sheets of metal are built up. During this  
30 process, alkali metal ions from the original alkali metal silicate particles are slowly dissolving, leading to the formation of alkali metal hydroxide in the aqueous phase.



When the water of the alkali metal silicate solution becomes locally supersaturated with respect to alkali metal hydroxide form and begin to grow, so that the interstitial material eventually becomes a dense mixture of  
5 alkali metal hydroxide crystals and aggregation of alkali metal silicate gel. At this stage, the morphology can no longer be clearly distinguished.

In ASP binding matrix that has set, this matrix has a very high surface area (i.e. several hundred  
10 m<sup>2</sup>/gr which clearly indicates a high porosity that is typical of a dehydrated gel.

Both alkali metal trisilicate and disilicate have an orthosilicate structure ( $2M_2O \cdot SiO_2$ ), consisting of a framework with channels large enough to admit of  
15 penetration by water molecules. Hydrolysis produces alkali metal cations and hydroxide anions which pass into the solution leaving orthosilicic acid on the surface of the alkali metal silicate crystal:



20 This suggests that the initial product of ASP grains surface is probably orthosilicic acid which will gradually polymerise to form a gel. This is followed by coagulation of the disilicate by alkali metal hydroxide, forming a membrane around the aggregated particle. As  
25 hydration continues at the surface of the particle the concentration of alkali metal cations in the solution inside the membrane rises, causing water to diffuse into the envelope under osmotic pressure, and eventually the membrane bursts open in several places releasing fresh  
30 disilicate anion  $(Si_2O_5)^{-2}$  which coagulates building a hollow tubular structure similar to a "silicate garden".

Following the initial set, there is a slow increase in strength over a longer period of time due to the slow polymerisation of the disilicate and trisilicate anions to higher polymers, increasing both in quantity and in molecular weight with time. Thus, the matrix which eventually binds the residual ASP cement particles together is a hydrated polysilicate glass.

This can provide an explanation of the effect of alumina in ASP cement. At the high Ph of ASP paste, any aluminum will be present in the form of aluminate anions from alkali metal trialuminate tetra hydrate ( $3M_2O \cdot Al_2O_3 \cdot MOH \cdot 12H_2O$ ) can be substitute as  $(Al_2O_7)^{-8}$  for some of the  $(Si_2O_5)^{-2}$  which present in  $(M_2Si_2O_5)$  in the polysilicate network.

This substitution produces an acid taste in the network which will accelerate the polycondensation reaction, causing a faster built-up of the covalent network and consequently a more rapid increase in mechanical strength for similar setting times.

The high heat and fire resistant properties of ASP materials are attributed to the formation of "catapleiite" such as Zirconyl alkali metal  $M_2ZrSi_2O_9 \cdot 2H_2O$  and/or the formation of "Erlonite-Chamosite" composite.

The following proportions of silico aluminous mineral materials are mixed uniformly with alkali metal silicate, sodium and/or potassium silicate and then mixed uniformly with all other ingredients with are set forth as well as the more specific and preferred proportions.

Description of preferred embodiments of the present invention

The preferred embodiments of the present invention are described hereunder in several examples using  
5 ranges of operable proportions of the several ingredients needed to reach the aim of the present invention.

Example 1 : Liquid component

Water, precipitated silica and alkali metal  
10 hydroxide such as potassium hydroxide and/or sodium hydroxide are charged into a stainless steel or PVC vessel equipped with a cover.

	Parts by weight	
	Range	Preferred embodiment
Potassium hydroxide	5 - 100	16.35
Precipitated silica SiO <sub>2</sub>	10 - 60	28.3
Water	30 - 70	55.35

The solution can be described as formula  
15  $K_2O.RSiO_2.XH_2O$ , in which R is designated to be the molar ratio of  $SiO_2/K_2O$  ranging from 0.5/1 to 9/1, and is preferably around 3.

The optimum  $SiO_2$  concentration as described in this example is 28.3 mass % with a modulus of 2.91 and  
20 of about 55 % water content.

During the initial mixing of these ingredients, evolution of heat raises the temperature of the content of the vessel in such a way that an exothermic reaction takes place over a period of time which may vary  
25 from two to three hours.

After the exothermic reaction, the contents are slowly cooled which may take another ninety minutes.

Example 2 : ASP matrix

	Parts by weight	
	Range	Preferred embodiment
Liquid component of example 1	5 - 25	15
Calcined clay of high silico aluminous minerals with $\text{Al}_6\text{Si}_2\text{O}_{13}\text{-Al}_2\text{O}_3$ . 4 $\text{SiO}_2$ of average particle size ranging from 50 to 70 microns	4 - 20	12
Zirconium silicate flour with particle size ranging from 50 to 70 microns	10 - 40	25
Pulverised raw materials of 40 to 80 wt % $\text{Al}_2\text{O}_3$ alumino content with grain size ranging from 80 to 500 microns	0 - 50	5

5

The product of this formulation exhibits properties such as :

- reversible thermal expansion 0.36 % (20 °C - 1150 °C)
- cold bending strength 6 MN/m<sup>2</sup>
- 10 - hot bending strength 5 MN/m<sup>2</sup> (at 1150 °C)
- water absorption 13 mass %
- hardness 9 Mohs

Example 3 : Liquid component

A solution is prepared in a manner similar to that described in example 1, except that it is made from the following ingredients :

	Parts by weight	
	Range	Preferred embodiment
Sodium hydroxide	3 - 100	11.1
Precipitated silica SiO <sub>2</sub>	10 - 80	27.7
Water	30 - 90	61.2

5

The solution can be described as formula  $\text{Na}_2\text{O} \cdot \text{R} \cdot \text{SiO}_2 \cdot \text{XH}_2\text{O}$ , in which R is designated to be the molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$  ranging from 0.5/1 to 9/1, and is preferably around 3,5.

10

The optimum SiO<sub>2</sub> concentration as described in the liquid component is 27.7 mass % with a modulus of 3.33 and about 61 % water content.

Example 4 : ASP matrix

	Parts by weight	
	Range	Preferred embodiment
Liquid component of example 3	5 - 25	18
Calcined clay of high silico aluminous minerals with $\text{Al}_6\text{Si}_2\text{O}_{13}\text{-Al}_2\text{O}_3$ . 4 $\text{SiO}_2$ of average particle size ranging from 50 to 70 microns	4 - 20	12
Zirconium silicate flour with particle size ranging from 50 to 70 microns	10 - 40	25
Pulverised raw materials with 40 to 80 wt % $\text{Al}_2\text{O}_3$ alumino content of grain size ranging from 80 to 500 microns	0 - 50	5

The product of this formulation exhibits properties such as :

- 5 - reversible thermal expansion 0.32 % (20 °C - 1150 °C)
- cold bending strength 5 MN/m<sup>2</sup>
- hot bending strength 4 MN/m<sup>2</sup> (at 1150 °C)
- water absorption 10 mass %
- hardness 9 Mohs

Example 5 : Liquid component

A solution is prepared in a manner similar to that described in example 1, except that it is made from the following ingredients :

	Parts by weight	
	Range	Preferred embodiment
Potassium hydroxide	5 - 100	23.7
Precipitated silica SiO <sub>2</sub>	10 - 60	23.7
Water	30 - 70	52.6

5

The solution can be described as formula  $K_2O.RSiO_2.XH_2O$ , in which R is designated to be the molar ratio of  $SiO_2/K_2O$  ranging from 0.5/1 to 9/1, and is preferably around 2.

10

The optimum SiO<sub>2</sub> concentration as described in the liquid component is 23.7 mass % with a modulus of 1.83 and about 53 % water content.

Example 6 : ASP matrix

	Parts by weight	
	Range	Preferred embodiment
Liquid component of example 5	5 - 25	15
Calcined clay of high silico aluminous minerals with Al <sub>6</sub> Si <sub>2</sub> O <sub>13</sub> -Al <sub>2</sub> O <sub>3</sub> . 4 SiO <sub>2</sub> of average particle size ranging from 50 to 70 microns	5 - 15	10

	Parts by weight	
	Range	Preferred embodiment
Zirconium silicate flour with particle size ranging from 50 to 70 microns	0 - 20	2
Pulverised raw materials with 40 to 80 wt % $\text{Al}_2\text{O}_3$ alumino content of grain size ranging from 80 to 500 microns	5 - 25	15

The product of this formulation exhibits properties such as :

- heat and fire resistance together with low thermal conductivity
- dry bending strength = 9 MN/m<sup>2</sup>
- dry compressive strength = 50 MN/m<sup>2</sup>
- wet bending strength = 9 MN/m<sup>2</sup>
- wet compressive strength = 48 MN/m<sup>2</sup>
- hardness = 8 Mohs.
- superior binding qualities when it is used as coating composition or reinforced by tiers

**Example 7 : Liquid component**

- 15 A solution is prepared in a manner similar to that described in example 1, except that it is made from the following ingredients :



	Parts by weight	
	Range	Preferred embodiment
Sodium hydroxide	3 - 100	21.3
Precipitated silica SiO <sub>2</sub>	10 - 80	26.4
Water	30 - 90	52.3

The solution can be described as formula Na<sub>2</sub>O.RSiO<sub>2</sub>.XH<sub>2</sub>O, in which R is designated to be the molar ratio of SiO<sub>2</sub>/Na<sub>2</sub>O ranging from 0.5/1 to 9/1, and is preferably around 1,6.

The optimum SiO<sub>2</sub> concentration as described in the liquid component is 26.4 mass % with a modulus of 1.61 and about 52 % water content.

10

Example 8 : ASP matrix

	Parts by weight	
	Range	Preferred embodiment
Liquid component of example 7	5 - 25	18
Calcined clay of high silico aluminous minerals with Al <sub>6</sub> Si <sub>2</sub> O <sub>13</sub> -Al <sub>2</sub> O <sub>3</sub> . 4 SiO <sub>2</sub> of average particle size ranging from 50 to 70 microns	5 - 15	10
Zirconium silicate flour with particle size ranging from 50 to 70 microns	0 - 20	2

	Parts by weight	
	Range	Preferred embodiment
Pulverised raw materials with 40 to 80 wt % $\text{Al}_2\text{O}_3$ alumino content of grain size ranging from 80 to 500 microns	5 - 25	15

The product of this formulation exhibits properties which are very similar to the product of example 6.

CLAIMS

1. A cementitious matrix consisting essentially of alumino silicate polymer comprising :

- a liquid component form of alkali metal silicate aqueous solution of formula  $M_2O.RSiO_2.XH_2O$ , in which :

M is an alkali metal monovalent cation such as  $K^+$  or  $Na^+$ ;

R is designated to be the molar ratio of  $SiO_2/M_2O$  range comprised between 0.5/1 and 9/1; and

X is the amount of water comprised between 30 and 70 wt%;

- a powder component form which comprises at least:

- silico-aluminous reactive raw materials composed of  $Al_6Si_2O_{13}$  and  $Al_2O_3.4 SiO_2$  with a relative proportion ranging from 40 to 60 wt%, the particle size of both components ranging from 50 to 70 microns.

2. A cementitious matrix according to claim 1, wherein the powder component further comprises zirconium silicate flour having a particle size ranging from 50 to 70 microns, the ratio of the zirconium silicate flour being comprised between 1 and 25 wt% of the total weight of the powder component.

3. A cementitious matrix according to claim 1 or 2, wherein the powder component further comprises pulverised raw materials being a combination of two major components which are:

- beauxite component having 80wt%  $Al_2O_3$  alumino content and having maximum grain size of 500 microns,

- chamosite component having 40wt%  $Al_2O_3$  alumino content and having an average grain size comprised

between 60 and 100 microns and being of the formula such as  $((\text{Fe}, \text{Al}, \text{Mg})_6 (\text{SiAl})_4 \text{O}_{10} (\text{OH})_8)$ , the combination of beauxite chamosite components wave ratio ranging from 1/1 to 1/2 and being preferably around 1/2,

5                   - the ratio of the raw materials being comprised between 1 and 25 wt% of the total weight of the powder component.

4. A cementitious matrix according to claim 3, further comprising alumino siliceous finely divided waste materials such as pulverised fuel ash.

5. A cementitious matrix according to claim 3 or 4, further comprising flake-like material such as Mica.

6. A cementitious matrix according to any of the claims 3 to 5, further comprising natural cellulose and protein base fibres such as flax, hemp and wool fibres.

7. A cementitious matrix according to any of the preceding claims, further comprising man-made organic and inorganic base fibres such as polyesters, polypropylene, glass and ceramic fibres.

8. A cementitious matrix according to any of the preceding claims, further comprising natural fibres of mineral origin.

9. A cementitious matrix according to any of the preceding claims, further comprising natural materials (heat treated) such as expanded perlite and vermiculite.

10. A cementitious matrix according to claim 1 or 2, further comprising synthetic raw materials possibly untreated such as crushed brick.

11. A cementitious matrix according to any of the claims 1 to 6, further comprising synthetic raw materials (treated) such as expanded polystyrene.

12. A cementitious matrix according to claim 3 or 4, further comprising silica sand and silica flour as filler.

5 13. A cementitious matrix according to claim 1 or 2, further comprising natural and synthetic organic base waste materials such as saw dust, rice husk and recycled organic waste.

14. A cementitious matrix according to claim 12, further comprising gas-forming agents such as  $H_2O_2$ .

10 15. A cementitious matrix according to claim 12, further comprising inorganic and organic colouring agents such as pigments.

16. A cementitious matrix according to claim 1 or 2, further comprising nominally inert materials such as pulverised limestone.

# INTERNATIONAL SEARCH REPORT

Intern. Application No  
PCT/BE 98/00099

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C04B28/00 C04B28/26

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 417 583 A (HULS TROISDORF AG) 20 March 1991 see the whole document	1,3-7, 12,14
A	US 4 642 137 A (LONE STAR INDUSTRIES, INC.) 10 February 1987 see claims	1
A	FR 2 169 864 A (USS ENGINEERS AND CONSULTANTS INC.) 14 September 1973 see page 2, line 26 - page 3, line 12	1
A	WO 93 21126 A (HULS TROISDORF AG) 28 October 1993 see column 5, line 21 - column 6, line 4 see page 7, line 33 - page 8, line 2; example	1,3-5,7, 9,12-14
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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Date of the actual completion of the international search

5 October 1998

Date of mailing of the international search report

12/10/1998

Name and mailing address of the ISA

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# INTERNATIONAL SEARCH REPORT

Intern. al Application No  
PCT/BE 98/00099

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>CHEMICAL ABSTRACTS, vol. 89, no. 26, 25 December 1978 Columbus, Ohio, US; abstract no. 219893q, XP000063944 see abstract &amp; JP 53 091929 A (NISSAN CHEMICAL INDUSTRIES LTD; NISSAN ENGINEERING CO., LTD)</p> <p>-----</p>	1,2,15

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Information on patent family members

International Application No

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